

XFM:

**A hard X-ray microprobe optimized
for EXAFS spectroscopy**

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XFM and NSLS's existing microprobe programs (X27A/X26A)

- The NSLS hard X-ray microprobes account for 6% of NSLS users (~150) annually with oversubscription rate of >250%.
- >100 publications over 5 years in peer-reviewed journals, and majority report X-ray Absorption Spectroscopy (μ XAS) measurements.
- **XFM** presents a direct opportunity to serve these science programs uninterrupted, and utilize the existing beamlines for pre-development.
- Existing X27A endstation remains state-of-the-art and will be incorporated into the **XFM** beamline
 - Complete EPICS-based control system and user interfaces (X26A/X27A have pioneered EPICS control at the NSLS and CARS is a key developer)
 - High-precision experimental stages and VME and cPCI controllers
 - State-of-the-art Energy Dispersive Detectors (HPGe and SDD arrays) and spectrometers (Maia and XMap)
 - CCD area detector (Bruker)

XFM Technical Overview

- **XFM** will provide variable spatial resolutions between 1-10 μm (plus 1mm macrofocus), accommodate samples up to meters in size, and provide a flux density two orders of magnitude higher than NSLS's existing microprobe beamlines.
- **XFM** will be optimized for microfocused Extended X-ray Absorption Fine Structure (μEXAFS) spectroscopy in the 4 to 20 keV range; NSLS-II's three-pole wigglers (3PW) are excellent sources for μEXAFS .
- **XFM** will exchange beam size and flux for a broadband source, sample configuration flexibility (e.g., large sample sizes and customized environmental chambers), and more readily achievable stability constraints for spectroscopies (μEXAFS).
- **XFM** will be complimentary to SRX (project beamline) and TES (NextGen beamline).

Techniques:

μ XRF imaging: '2-D' localization/ associations

μ XRF tomography (fCMT): '3-D' localization/
associations

μ XAS (EXAFS & XANES):

XANES - fingerprint information/ valence state

EXAFS - short-range order/ speciation

μ XRD: phase identification (~crystalline)

Beamline Performance:

Source	3-pole wiggler σ_h (μm) = 167, σ_v (μm) = 12.3
Energy range	4 – 20 keV
Monochromator	Si(111), Si(311) 1.2×10^{-4} , 2.5×10^{-5} ($\Delta E/E$)
Flux (on sample)	2×10^{11} @ 9keV (10x5 μm spot) 3×10^9 @ 9keV (1x1 μm spot)
Spot size	zoomable 1x1 μm to 10x5 μm macrofocus 1x1 mm

Optimized? for spectroscopy?

- Electron beam size ~5X larger than low-B straight (i.e., not optimized for imaging)

Table 2. Electron Beam Size and Divergence at NSLS-II

Type of source	Low-Beta Straight Section (6.6m)	High-Beta Straight Section (9.3m)	0.4T Bend Magnet	1T Three-Pole Wiggler
σ_h (μm)	33.3	107	125	167
σ_h' (μrad)	16.5	5.1	91	98
σ_v (μm)	2.9	5.2	13.4	12.3
σ_v' (μrad)	2.7	1.5	0.80	0.82

Optimized? for spectroscopy?

- Broadband source flux $\sim 10^2$ lower than peak intensities for IDs

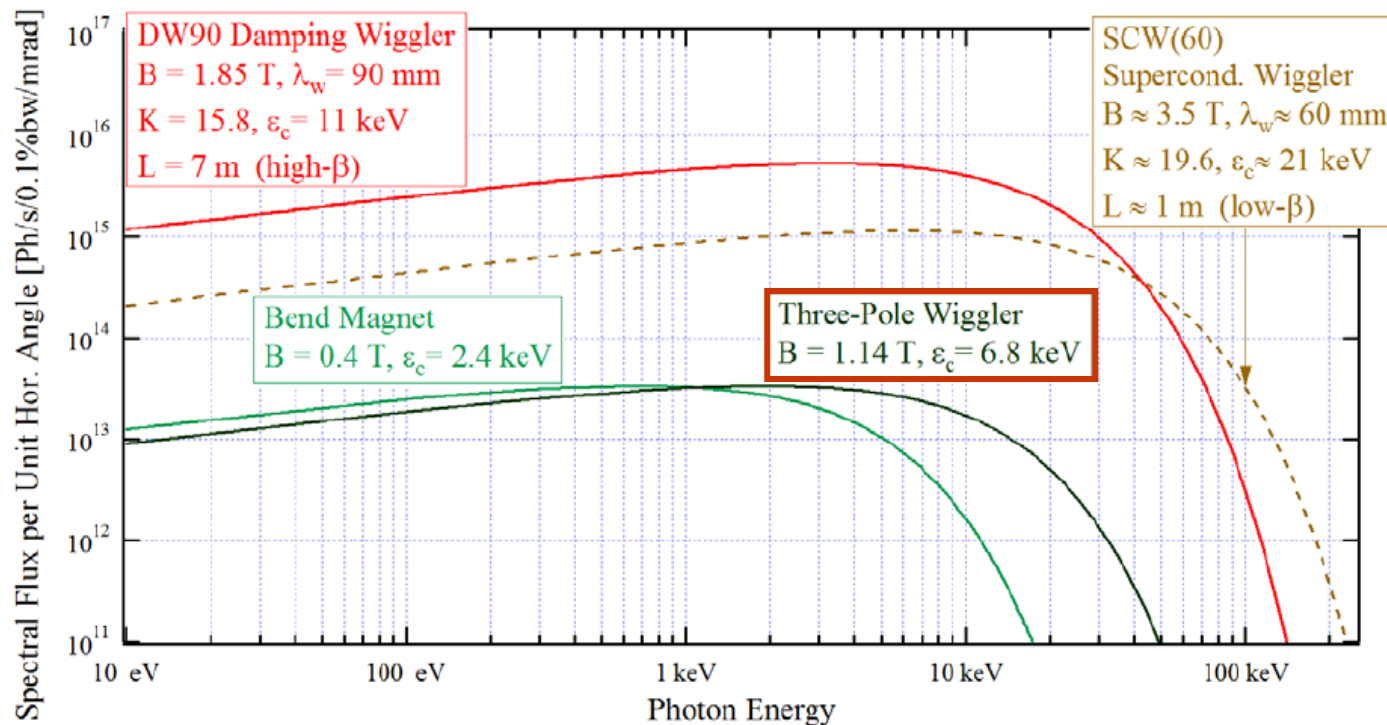
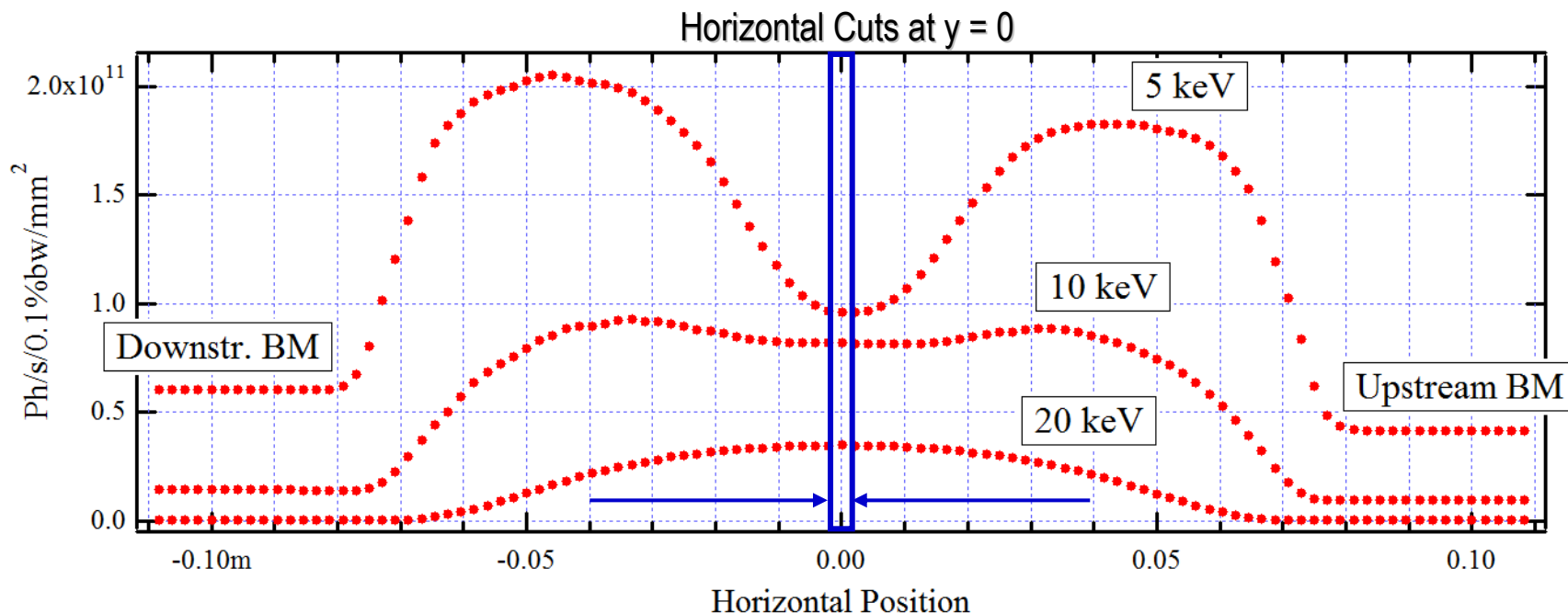


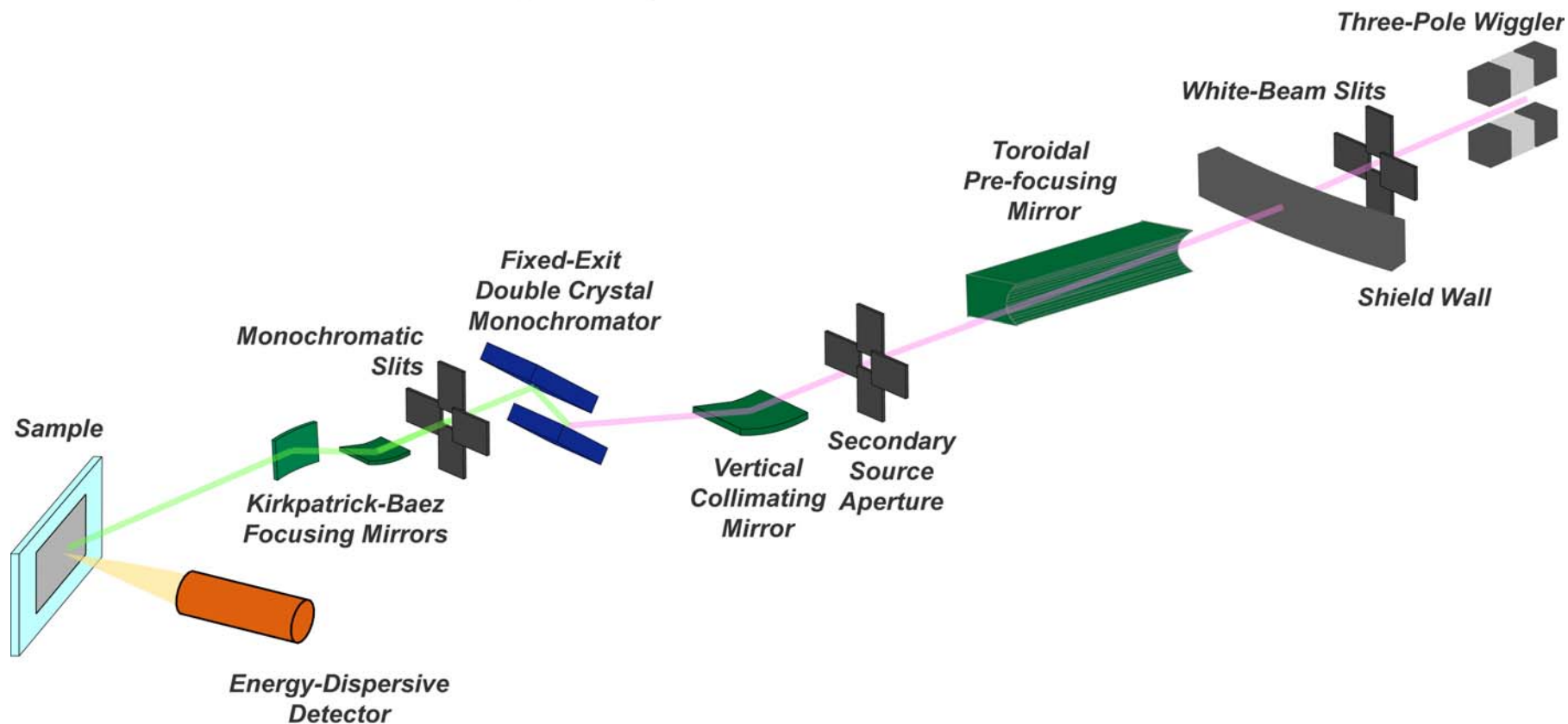
Figure 3. Spectral flux versus photon energy for a number of different NSLS-II wiggler and bend-magnet sources, at 3 GeV and 500 mA.

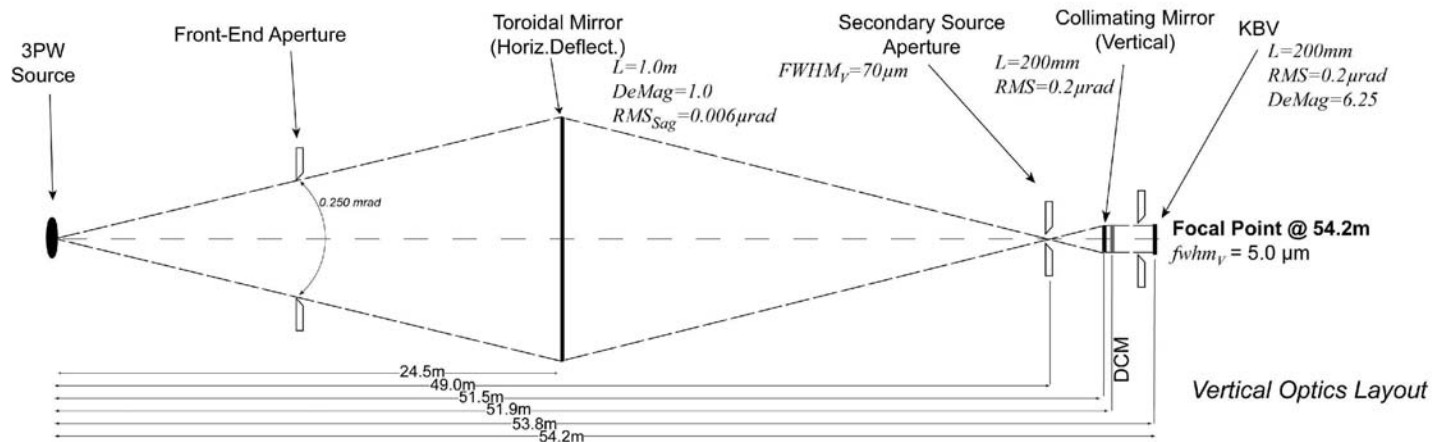
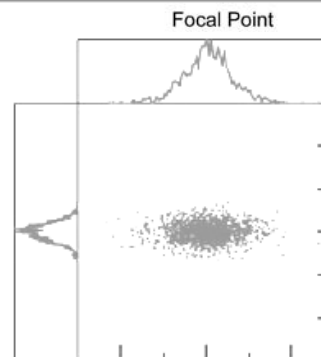
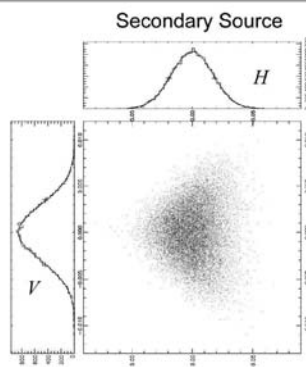
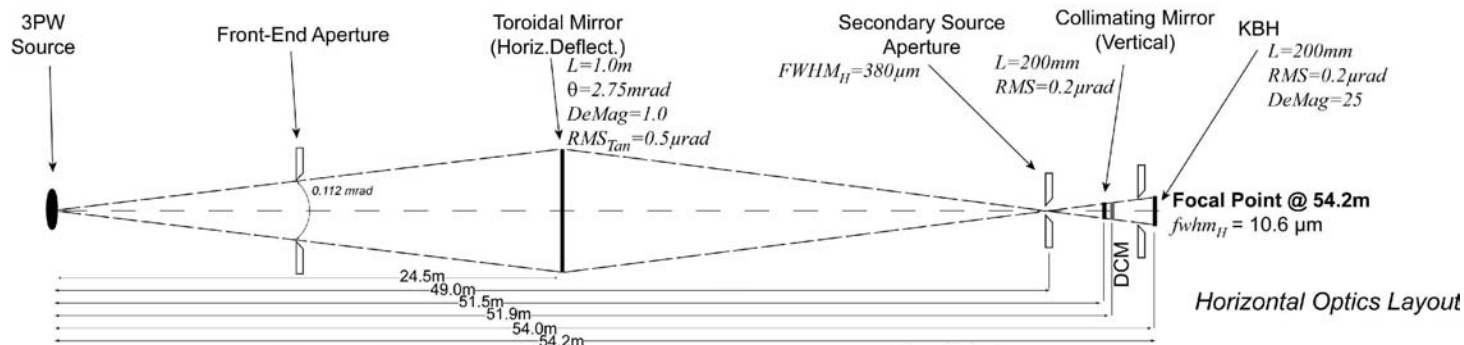
Optimized? for spectroscopy?

- Intensity distributions at different photon energies at 30 m from 3PW



Central 0.112 mrad horizontal fan (plus full 0.25 mrad vertical fan) defined by M1 (torroid) acceptance; preferentially accepts radiation from central pole of 3PW.

NSLS-II**XFM Versatile Hard X-ray Microprobe**



Energy	Source flux (0.33HxfullV)	Flux at sample position*		
keV	Ph/s/0.1%bw	10 x 5 μm	5 x 5 μm	1 x 1 μm
4	1.1E+13	2.E+11	8.E+10	3.E+09
5	9.5E+12	2.E+11	1.E+11	4.E+09
6	8.8E+12	2.E+11	1.E+11	4.E+09
7	8.0E+12	2.E+11	9.E+10	4.E+09
8	7.2E+12	2.E+11	9.E+10	4.E+09
9	6.5E+12	2.E+11	8.E+10	3.E+09
10	5.8E+12	1.E+11	7.E+10	3.E+09
11	5.1E+12	1.E+11	6.E+10	3.E+09
12	4.6E+12	1.E+11	6.E+10	2.E+09
13	4.1E+12	1.E+11	5.E+10	2.E+09
14	3.6E+12	9.E+10	5.E+10	2.E+09
15	3.3E+12	8.E+10	4.E+10	2.E+09
16	3.0E+12	8.E+10	4.E+10	2.E+09
17	2.6E+12	7.E+10	3.E+10	1.E+09
18	2.4E+12	6.E+10	3.E+10	1.E+09
19	2.2E+12	6.E+10	3.E+10	1.E+09
20	2.0E+12	5.E+10	3.E+10	1.E+09
*Fixed aperture (0.112 x 0.25 mrad); Si(111) bandpass; 12.5 μm Be window; 5 cm air absorption				

On-sample beam sizes with secondary source aperture fully open to 36 x 14 microns (10 x 5 μm spot) or closed down for smaller spot size

XFM comparison to other microprobes/nanoprobes			
Beamline	Energy range (keV)	Spot size (μm^2)	Max Photon flux in spot
XFM @ NSLS-II	4 - 20	1 x 1 – 10 x 5	2×10^{11}
X26A @ NSLS	4.5 - 20	6 x 5	2×10^9
X27A @ NSLS	4.0 - 30	14 x 7	5×10^9
10.3.2 @ ALS	3 - 17	5 x 5 - 16 x 7	9×10^9
BM05/29 @ ESRF	6 - 13	1.5 x 1.4	2.5×10^7
SRX @ NSLS-II	4.65 – 25.0	0.5 x 0.5 0.05 x 0.05	$> 10^{13}$ $> 10^{11}$
ID21 @ ESRF	2 - 7.5	0.2 x 0.2 - 1 x 1	$10^8 - 10^9$
ID22 @ ESRF	6.5 - 18	3.5 x 1.5	10^{12}
2-ID-B @ APS	2 - 4	0.06 x 0.06	10^9
2-ID-D @ APS	5 - 30	0.2 x 0.2	4×10^9
2-ID-E @ APS	7.5 - 10	0.5 x 0.3	5×10^9
13-ID-C,D @ APS	4 - 45	2 x 2	10^{11}
20-ID-B,C @ APS	4.3 - 27	2 x 2	10^{11}
XFM @ AS	4 - 25	0.06 x 0.06	10^{10}
MicroXAS @ SLS	5 - 20	1 x 1	2×10^{12}
LUCIA @ SOLEIL	0.8 - 8	2.5 x 2.5	2×10^{11}

XFM will provide spatially-resolved characterization of elemental abundances and speciation in samples that are heterogeneous at the micrometer scale

Principal Science Areas

- Genetic Control of Metal Ion Uptake, Transport and Storage in Plants Relevant to Agriculture and Bioenergy
- Biogeochemistry of Nanotoxins in the Environment
- Molecular Speciation of Contaminants in the Environment at the Microscale
- Metal Ions in Health and Disease
- Mineral-fluid Interface Reactions Relevant to Carbon Sequestration
- Early Solar System Properties Inferred through Analysis of Extraterrestrial Materials
- Characterization of Paleontological, Archeological and Cultural Heritage Artifacts.

Periodic table highlighting X-ray fluorescence

□ K-line Fluorescence typically used □ L-line Fluorescence typically used

Major/minor elements in Biological Systems

,Natural' Trace elements

Toxic / carcinogenic elements

Used in Imaging, Diagnosis, Therapy, ...

★ Geochemically Important

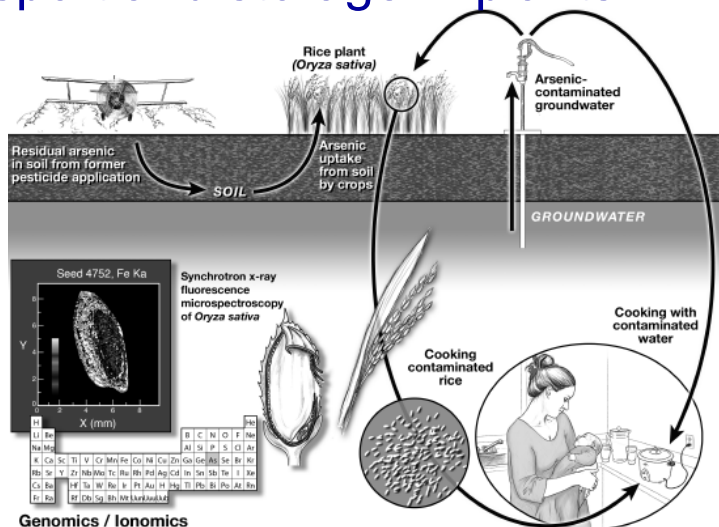
1	H★	2	He
3	Li★	4	Be★
5	B★	6	C★
7	N★	8	O★
9	F★	10	Ne
11	Na★	12	Mg★
13	Al	14	Si★
15	P★	16	S★
17	Cl★	18	Ar
19	K★	20	Ca★
21	Sc	22	Ti
23	V★	24	Cr★
25	Mn★	26	Fe★
27	Co★	28	Ni★
29	Cu★	30	Zn★
31	Ga	32	Ge
33	As★	34	Se★
35	Br★	36	Kr
37	Rb	38	Sr
39	Y	40	Zr
41	Nb	42	Mo★
43	Tc	44	Ru
45	Rh	46	Pd
47	Ag	48	Cd
49	In	50	Sn
51	Sb★	52	Te★
53	I★	54	Xe
55	Cs	56	Ba
57	La	58	Ce
59	Pr	60	Nd
61	Pm	62	Sm
63	Eu	64	Gd★
65	Tb	66	Dy
67	Ho	68	Er
69	Tm	70	Yb
71	Lu	72	Hf
73	Ta	74	W★
75	Re	76	Os★
77	Ir	78	Pt★
79	Au★	80	Hg★
81	Tl	82	Pb★
83	Bi★	84	Po
85	At	86	Rn★
87	Fr	88	Ra
89	Ac	90	Th
91	Pa	92	U
93	Np	94	Pu★
95	Am	96	Cm
97	Bk	98	Cf
99	Es	100	Fm
101	Md	102	No

Genetic control on metal transport and storage in plants

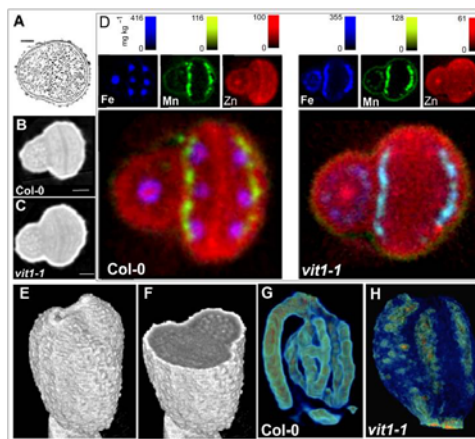
- **XFM** is well-suited for evaluation of how specific genes influence the uptake of nutrients and contaminants in plants

- fCMT provides non-destructive, three dimensional characterization of elemental distribution in plants *in vivo*. fCMT images of knockout and WT *Arabidopsis* seed confirmed localization of Fe requires vacuolar membrane transporter VIT1.

- μ XRF imaging and μ XANES were used to evaluate the chemical form of As in edible rice grain, which determines its bioavailability and toxicity.



Oryza sativa drawing and synchrotron x-ray fluorescence microspectroscopy by Tracy Punshon. All other images ©2007 William Scavone. All rights reserved.

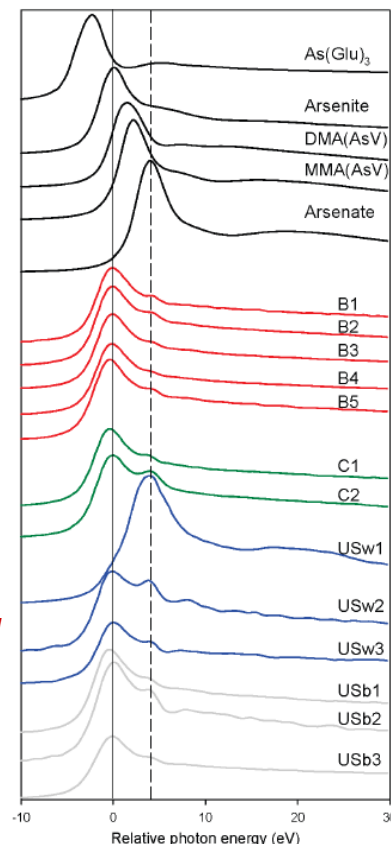


Kim, et al., Science, 2007

Punshon, et al., 2008

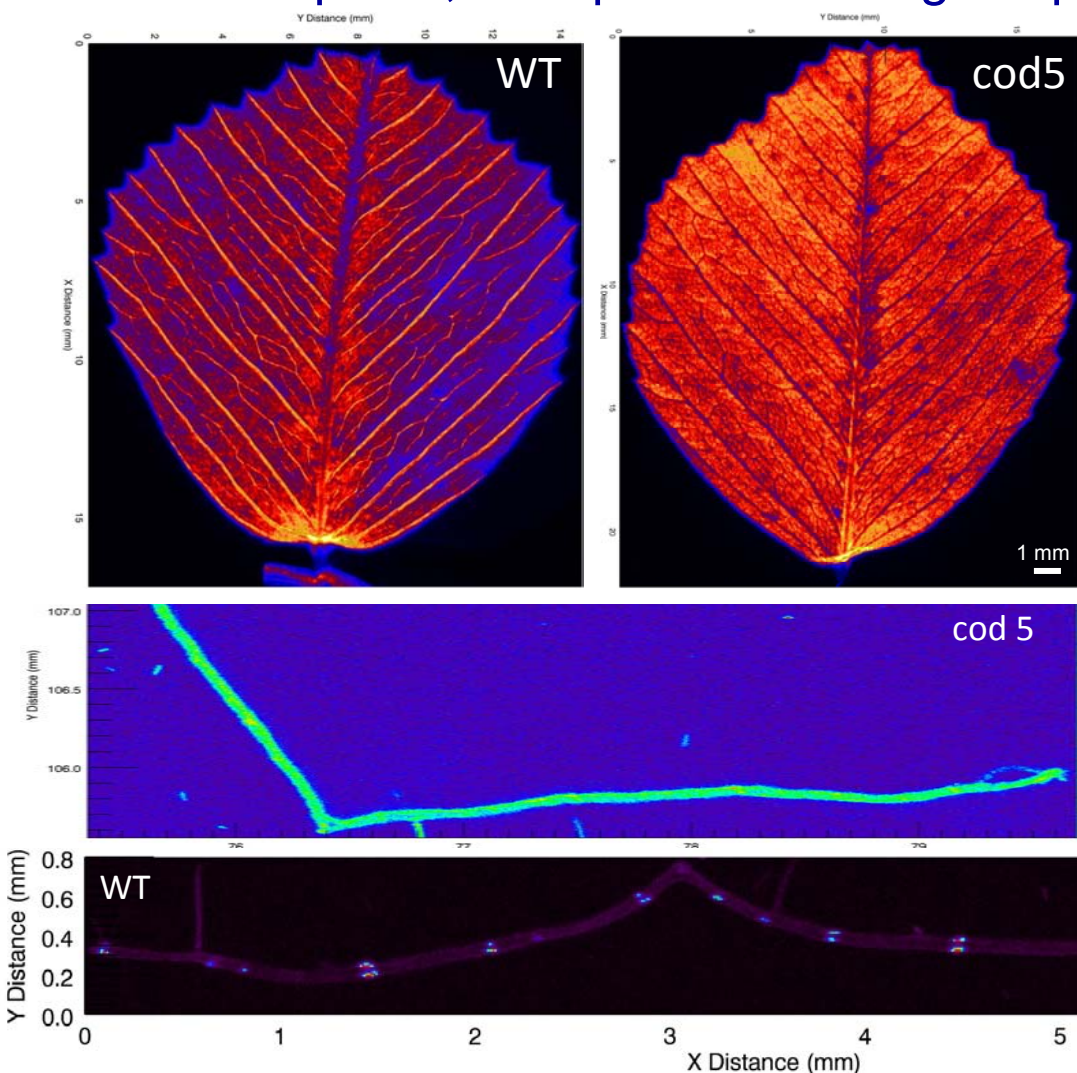
3D in-vivo imaging of metals in *Arabidopsis* using fluorescence microtomography

As XANES spectroscopy from rice



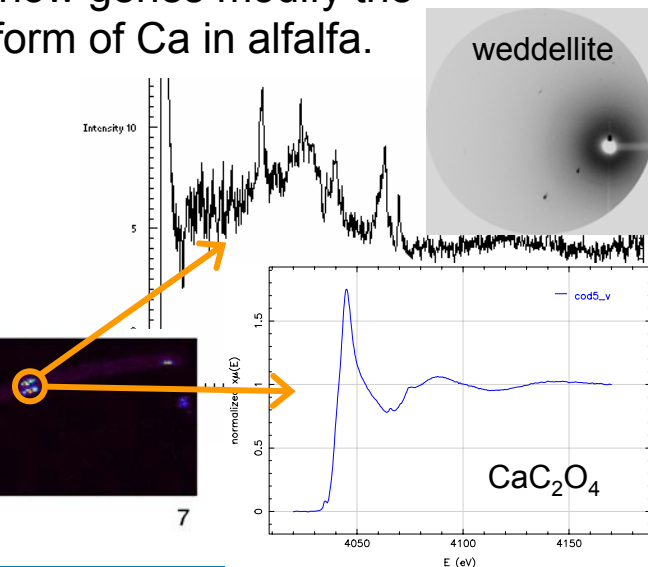
Meharg et al., ES&T, 2008

Metal ion uptake, transport and storage in plants: Biofortification of crops



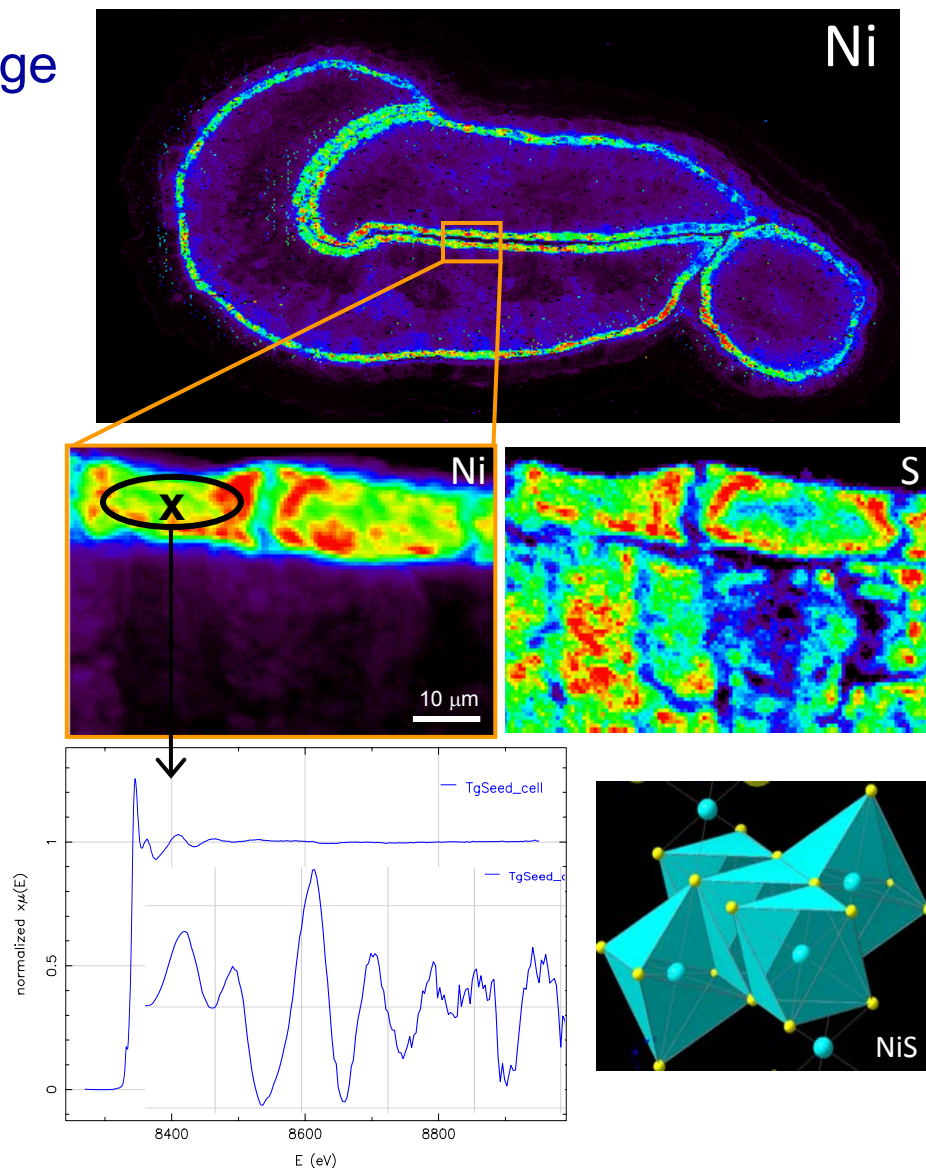
- Calcium (Ca) abundance is not linked directly to Ca bioaccessibility because mineral forms (e.g., CaC_2O_4 , weddellite) are not readily absorbed. Crop plants can be modified to contain more bioaccessible Ca (biofortification).

- μXRF , μXANES , μXRD were used to study how genes modify the storage form of Ca in alfalfa.



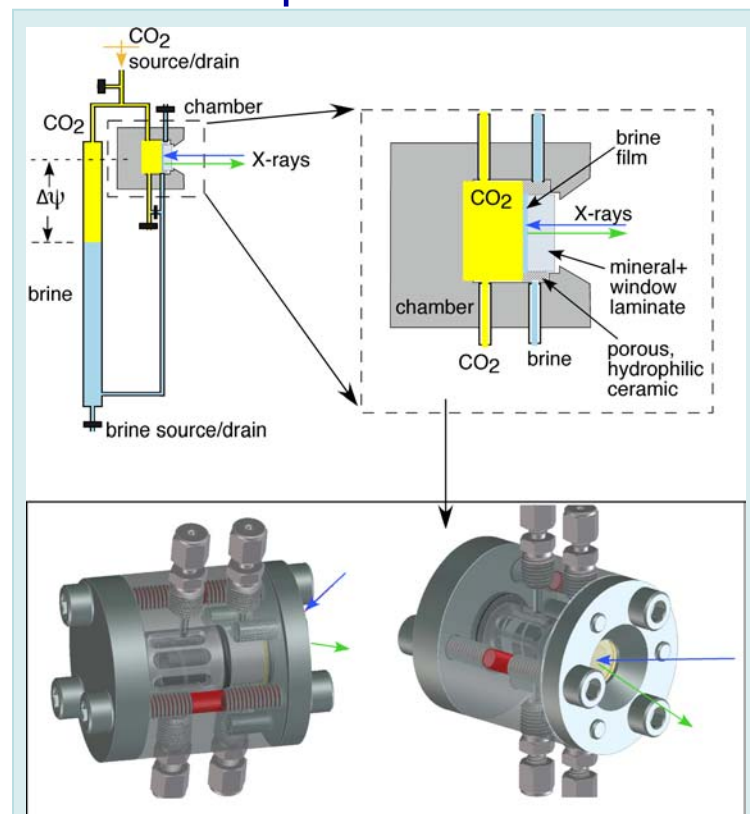
Metal ion uptake, transport and storage in plants: Phytoremediation

- Hyperaccumulator plants can be used to recover metals of economic value from enriched or contaminated soils.
- Mechanisms of metal tolerance as well as metal ion uptake, transport, and storage in plants are being studied to improve understanding of hyperaccumulation.
- **XFM**'s strengths in μ EXAFS can help evaluate the chemical forms of metals *in vivo* to understand the underlying mechanisms.
- Complemented by the higher resolution imaging of NSLS-II's undulator-based probes (sub-cellular characterization).



Mineral-fluid Interface Reactions Relevant to Carbon Sequestration

- When supercritical CO₂ displaces brine from rock pores, films of residual brine remain adsorbed on mineral surfaces and mediate transport and reactions.
- Determining hydraulic properties of brine films requires testing under scCO₂ confinement ($T > 31^{\circ}\text{C}$, $P > 7.4\text{ MPa}$), while controlling ΔP . This requires *in-situ* XRF and XRD analysis within high-P experimental cells (i.e. 'large' environmental chambers).
- **XFM** will utilize *in-situ* XRF (measure tracer concentration), XAS (speciation *in situ* along the grain surfaces) and XRD (visualize change in pore volume and mineralogy) to quantify hydraulic/transport properties of brine films confined by CO₂ under geologically relevant conditions.

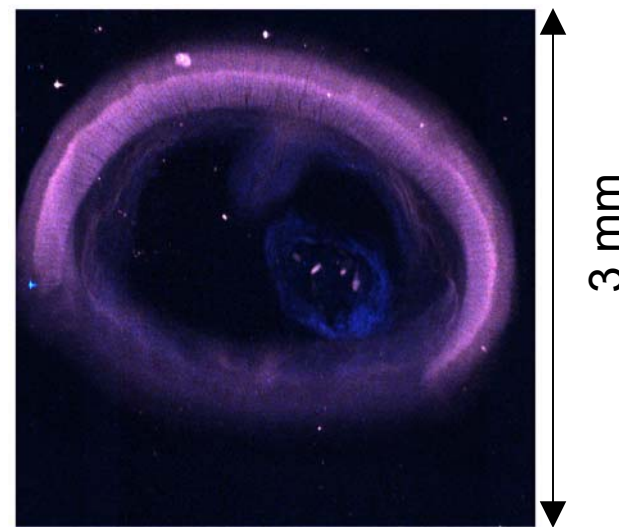


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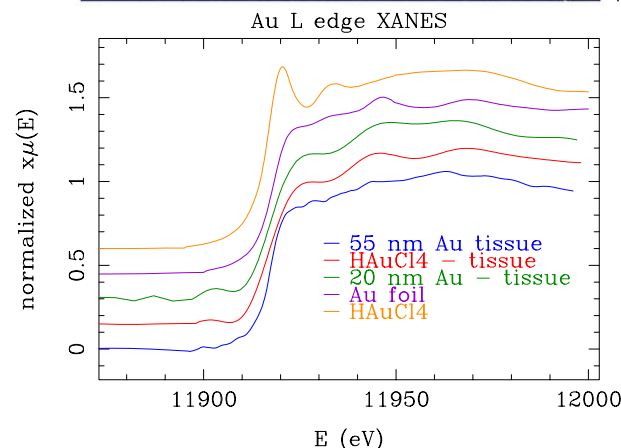
Biogeochemistry of Nanotoxins in the Environment

- μ XRF and μ XAFS allows evaluation of the fate, transport, and toxic effects of manufactured nanoparticles in the environment.
- Requires characterization in soil & biota, along mineral grains & fractures, pore linings, plant root/soil interfaces, and at mm length scales.
- μ EXAFS will allow differentiation of metallic nanoparticles from ions and characterization of their molecular transformations within organisms.
- X-ray microprobes have provided some of the first conclusive evidence that nanomaterials are bioavailable to soil organisms.
- Further characterization at sub- μ m resolution using SRX.



Earthworm
cross-section
Blue=Au L α 1
Pink=Zn K α

3 mm



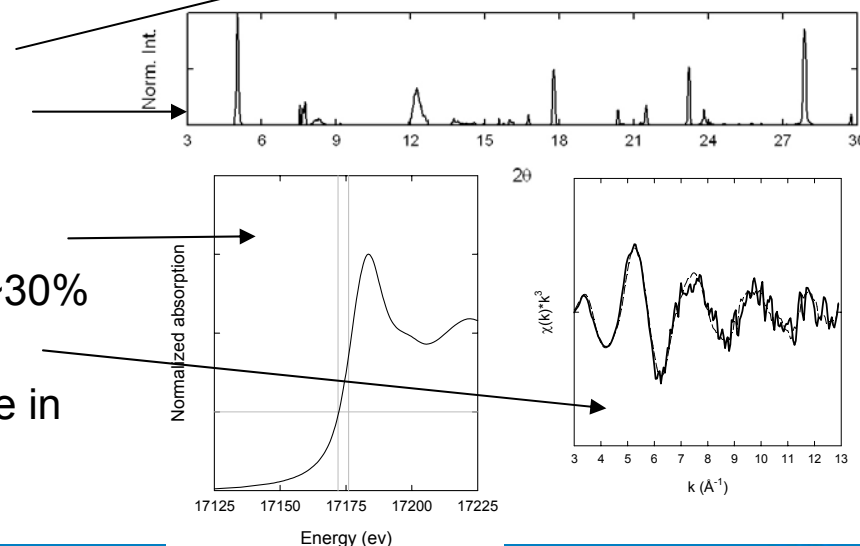
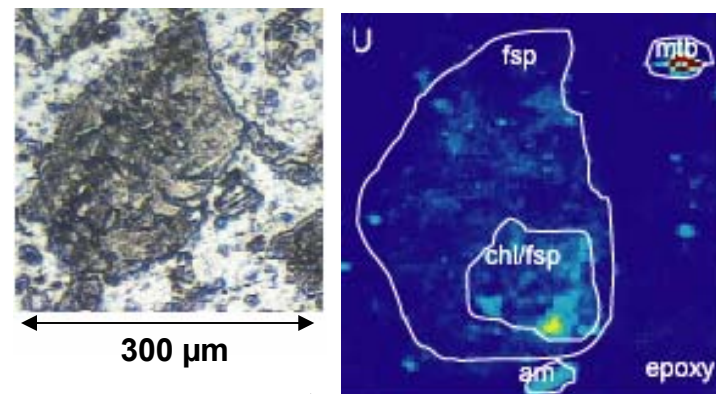
*Judy, Unrine,
Bertsch. ES&T*

Earthworms exposed to 25 mg kg⁻¹ HAuCl₄ or 50 mg kg⁻¹ Au NPs in OECD soil media for 28 d. Tissue Au < 1 mg kg⁻¹

Molecular Speciation of Contaminants: U in Hanford Sediments (Area 300)

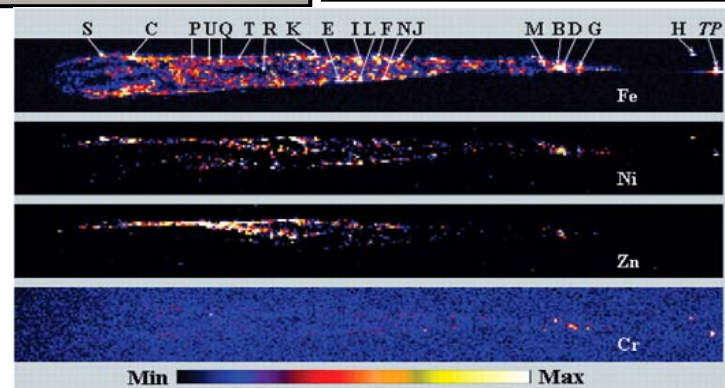
D. Singer, J. Zachara, G. E. Brown, Jr. (2009) ES&T 43 (3), 630-636

- Depth-dependent study using micro-XRF, -XANES, -XRD and bulk EXAFS
- Contaminated sediments from the Hanford 300 Area were collected from one (NPP2) of four vertical excavations in the 300 Area Processing Pond complex.
- Define geochemical processes that now control U-fluxes within the saturated zone.
 - μ XRF – U heterogeneous at μm -scale
 - μ XRD – U associated with chlorite grain coatings and U-Cu-phosphates
 - μ XANES – Dominant valence state U(VI)
 - Bulk EXAFS – e.g., 70% sorbed to clay, ~30% precipitated as U-Cu-phosphates
 - μ EXAFS – not done but would be valuable in confirming speciation partitioning



- **XFM**: methods for analyzing extraterrestrial samples in an “as-collected” state.
- Conditions (X , fO_2 , T , etc.) at the earliest stages of Solar System.
- Samples: Moon, Mars, asteroids, comets, solar wind, interstellar grains
- Wide range in sizes
- Mineralogic components often $< 1 \mu\text{m}$ in size
- Need to determine elemental composition and speciation at trace levels and mineralogy *in-situ* at range of scales down to sub-micrometer.
- Stardust comet particles contain abundant high-temperature minerals \Rightarrow material formed in the inner solar system has been transported to $\approx 40 \text{ AU}$

Lanzirotti, A., et al. (2008) *Meteoritics & Planetary Science*, 43, 187-214



Characterization of Paleontological, Archeological & Cultural Heritage Artifacts

- **XFM** provides a unique platform for non-invasive micro-beam characterization of large corpuses (high throughput) and unique, high-value artworks in the as-is state:

- In-situ XRF and XRD analysis of heterogeneous historical objects
- Chemical forensics, chemical and mineralogical changes for conservation, elemental distribution related to a large fossilized organism's life processes
- Variable resolutions between 1 μm and 1 mm using focused and collimated beams
- Long working/travel distance accommodating samples m's in size
- Unique, next-generation high-speed fluorescence detectors



NSLS-II needs XFM...

← 60 000 μm !!! →

COMING SOON
(in 3-D)!

